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The Interstellar Oxygen Crisis, or Where Have All the Oxygen Atoms Gone?*

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ABSTRACT
The interstellar medium (ISM) seems to have a significant *surplus* of oxygen which was dubbed as the "O crisis": independent of the adopted interstellar reference abundance, the total number of O atoms depleted from the gas phase far exceeds that tied up in solids by as much as ~ 160 ppm of O/H. Recently, it has been hypothesized that the missing O could be hidden in micrometer-sized H_2O ice grains. We examine this hypothesis by comparing the infrared (IR) extinction and far-IR emission arising from these grains with that observed in the Galactic diffuse ISM. We find that it is possible for the diffuse ISM to accommodate ~ 160 ppm of O/H in μm-sized H_2O ice grains without violating the observational constraints including the absence of the 3.1 μm O–H absorption feature. More specifically, H_2O ice grains of radii $\sim 4\,\mu$m and O/H = 160 ppm are capable of accounting for the observed flat extinction at ~ 3–$8\,\mu$m and produce no excessive emission in the far-IR. These grains could be present in the diffuse ISM through rapid exchange of material between dense molecular clouds where they form and diffuse clouds where they are destroyed by photosputtering.

Key words: dust, extinction – infrared: ISM – ISM: abundances

1 INTRODUCTION

The depletion of certain heavy elements from the interstellar gas, known as the "interstellar depletion", was first noticed by Morton et al. (1973) who found that the gas-phase abundances of these elements measured by the *Copernicus* ultraviolet (UV) satellite for interstellar clouds are significantly lower than in the Sun. Based on the strong correlation between the depletions of these elements and the condensation temperatures at which they are incorporated into solid grains in stellar atmospheres and nebulae, Field (1974) proposed that the elements missing from the gas phase must have condensed into dust grains.

Assuming the interstellar reference abundances to be the same as the accepted solar abundances at the time (Cameron 1973), Greenberg (1974) compared the observed interstellar depletions with the abundances of the dust-forming elements required to account for the observed visual extinction. He found that a substantial amount of the intermediate-weight elements O, C, and N was unaccounted for by the interstellar gas and dust whereas the heavier elements Si, Mg and Fe were underabundant.

Snow & Witt (1996) compiled the elemental abundances of early B stars and young F and G stars and found that their abundances are just ~ 50–70% of the then accepted solar abundances of Anders & Grevesse (1989). They argued that, due to their young ages, the photospheric abundances of unevolved B stars and young F and G stars are more representative of the interstellar composition than the 4.6-billion-year-old Sun. If the interstellar abundances are indeed subsolar, the original question of a surplus of missing, unaccountable elements posed by Greenberg (1974) then turned into a shortage of raw materials for making the dust to account for the observed extinction. This was most pronounced for carbon. Whereas published values for the Sun range from $[\mathrm{C/H}]_\odot \approx 350$ ppm to ≈ 470 ppm, where ppm stands for parts per million, Snow & Witt (1995) derived a C/H abundance of ~ 225 ppm for Galactic stars. With the gas-phase abundance of $[\mathrm{C/H}]_{\mathrm{gas}} \approx 140$ ppm (Cardelli et al. 1996) or ≈ 100 ppm (Sofia et al. 2011)[1] subtracted, the remaining C/H abundance of ~ 85 ppm or ~ 125 ppm is in-

* Dedicated to the late Professor J. Mayo Greenberg (1922.1.14–2001.11.29) of Leiden University who suggested the possible existence of interstellar snowballs four decades ago.

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[1] Jenkins (2014) argued that the gas-phase C/H abundance of Sofia et al. (2011) derived from the strong transition of C II at 1334 Å may be more trustworthy than the previous values mea-

sufficient to form the carbonaceous dust required by all dust models. This, known as the "C crisis", still holds when one compares the most recent determinations of the solar abundance of C/H $\approx$ 269 ppm (Asplund et al. 2009) and early B stars of C/H $\approx$ 214 ppm (Nieva & Przybilla 2012)[2] with the latest dust models (e.g., Jones et al. 2013) which all require $[\mathrm{C/H}]_{\mathrm{dust}} > 200$ ppm to be locked up in carbonaceous dust. Note that the refined studies of the solar abundances since Anders & Grevesse (1989) all led to a gradual, downward revision such that the derived solar abundances were no longer substantially higher than that of B stars, and hence the C crisis remains unalleviated with the new solar and B-star abundances. It is worth noting that Lodders (2003) argued that the currently observed solar photospheric abundances must be lower than those of the proto-Sun because heavy elements have settled toward the Sun's interior since the time of the Sun's formation some 4.6 Gyr ago. She further argued that the protosolar abundances are more representative of the solar system elemental abundances.

The depletion of oxygen is also problematic. Unlike C of which the depletion is insufficient to account for the observed extinction, the major solid-phase reservoirs of O in the diffuse interstellar medium (ISM) — silicates and metal oxides — are insufficient to account for the total O/H abundance missing from the gas phase. Jenkins (2009) examined the relative proportions of 17 individual elements that are incorporated into dust along 243 different Galactic sightlines. He found that the depletion of O in the diffuse ISM far exceeds the consumption of O by silicates and metallic oxides, except for low-density regions with little depletions. This is insensitive to the adopted reference abundance since the approach taken by Jenkins (2009) was based on differential depletions rather than absolute values. Whittet (2010b) investigated the depletions of O over a wide range of environments from the tenuous intercloud medium and diffuse clouds to dense clouds where H_2O ice is present. He found that as much as ~ 160 ppm of O/H is unaccounted for at the interface between diffuse and dense phases, again, independent of the choice of reference abundances. This surplus of O, dubbed as the interstellar "O crisis" by Whittet (2010a), poses a severe challenge to our understanding of interstellar dust.

The nondetection of the 3.1 μm O–H stretching absorption feature of H_2O ice in the diffuse ISM rules out submicrometer-sized H_2O ice grains as a significant reservoir of O (Whittet et al. 1997, Poteet et al. 2015). Jenkins (2009) suggested that large amounts of O could be hidden in H_2O ice grains (or large grains with thick mantles of H_2O ice) that have diameters of the order of or greater than 1 μm. Grains this large will have the 3.1 μm O–H feature substantially suppressed.[3] More recently, Poteet et al. (2015) analyzed the $\sim$ 2.4–36 μm absorption spectrum of the sightline toward ζ Ophiuchi obtained with the *Short Wavelength Spectrometer* (SWS) on board the *Infrared Space Observatory* (ISO) and the *Infrared Spectrograph* (IRS) on board the *Spitzer Space Telescope*. They determined the elemental abundances of O, Mg, and Si in silicates. Along with the upper limit estimates of O in other materials, they found that as much as $\sim$ 156 ppm of O/H is unaccounted for along the line of sight toward ζ Ophiuchi, a prototypical cool diffuse cloud and an environment near the diffuse-dense ISM transition. They argued that the missing reservoir of O must reside on very large, micrometer-sized grains (e.g., with radii $a \gtrsim 3.2\,\mu$m) which are nearly opaque to infrared (IR) radiation.

The aim of this work is to test the hypothesis of μm-sized H_2O ice grains as the repository of the unaccounted for $\sim$ 160 ppm of O/H in the diffuse ISM. Roughly speaking, dust scatters and absorbs starlight most effectively at a wavelength λ comparable to its spherical radius a: $4a(n-1)/\lambda \sim 1$, where $n(\lambda)$ is the real part of the index of refraction of the dust. This can be understood in terms of elementary optics: the maxima of the extinction could be considered as being caused by the destructive interference between the incident and forward-scattered light. The phase difference between a ray that traverses a large transparent sphere without deviation (i.e., the forward-scattered ray) and a ray that traverses the same physical path outside the sphere is $\Delta\phi = (2\pi/\lambda)\,2a(n-1)$. The maxima of the extinction occur at $\Delta\phi = (2j+1)\pi$, where j is an integer, with $j = 0$ corresponding to the principal extinction peak (see Bohren & Huffman 1983).

For H_2O ice, $n \approx 1.3$ at $\lambda \gtrsim 1\,\mu$m (Warren 1984), thus, μm-sized H_2O ice grains will cause extinction at $\lambda > 1\,\mu$m. Therefore, we will examine in §2 the consistency between the observed IR extinction and the extinction resulting from the standard silicate-graphite model with the addition of a population of μm-sized H_2O ice grains of O/H = 160 ppm. On the other hand, H_2O ice grains are transparent in the ultraviolet (UV) and visible wavelength range and hence they will be cold and emit in the far-IR at $\lambda \gtrsim 200\,\mu$m. Therefore, we will examine in §3 the IR radiation emitted by μm-sized H_2O ice grains and make a comparison between the model IR emission and that observed for the Galactic diffuse ISM. Their origin and survival will be discussed in §4. The major conclusions are summarized in §5.

2 EXTINCTION

For H_2O ice grains to be considered as a viable component of the diffuse ISM, they should satisfy the constraints placed by the observed extinction from the far-UV to the IR, including the absence of the 3.1 μm absorption feature of H_2O ice. The observed UV/optical interstellar extinction can be characterized by a single parameter R_V (Cardelli et al. 1989, CCM).[4] As elaborated in Wang, Li & Jiang (2014), while the UV/optical extinction can be closely fitted by the classical silicate-graphite model (Mathis et al. 1977, Draine & Lee 1984), this model predicts a power-law of $A_\lambda \propto \lambda^{-1.75}$ at

sured from the weak intersystem absorption transition of C II] at 2325 Å.

[2] Poteet et al. (2015) found that the B-star Si and Mg abundances are not enough to account for the 9.7 μm Si–O absorption feature observed toward ζ Ophiuchi (see their Figure 8).

[3] As illustrated in Figure 4 of Poteet et al. (2015), for 2.0–3.2 μm-sized H_2O ice grains, with increasing grain size, both the scattering and absorption at the 3.1 μm O–H stretch decrease.

[4] $R_V \equiv A_V/(A_B - A_V)$ is the total-to-selective extinction ratio, where A_B and A_V are the blue- and visual-band extinction at $\lambda_B = 4400$ Å and $\lambda_V = 5500$ Å, respectively. For the Galactic average, $R_V \approx 3.1$.

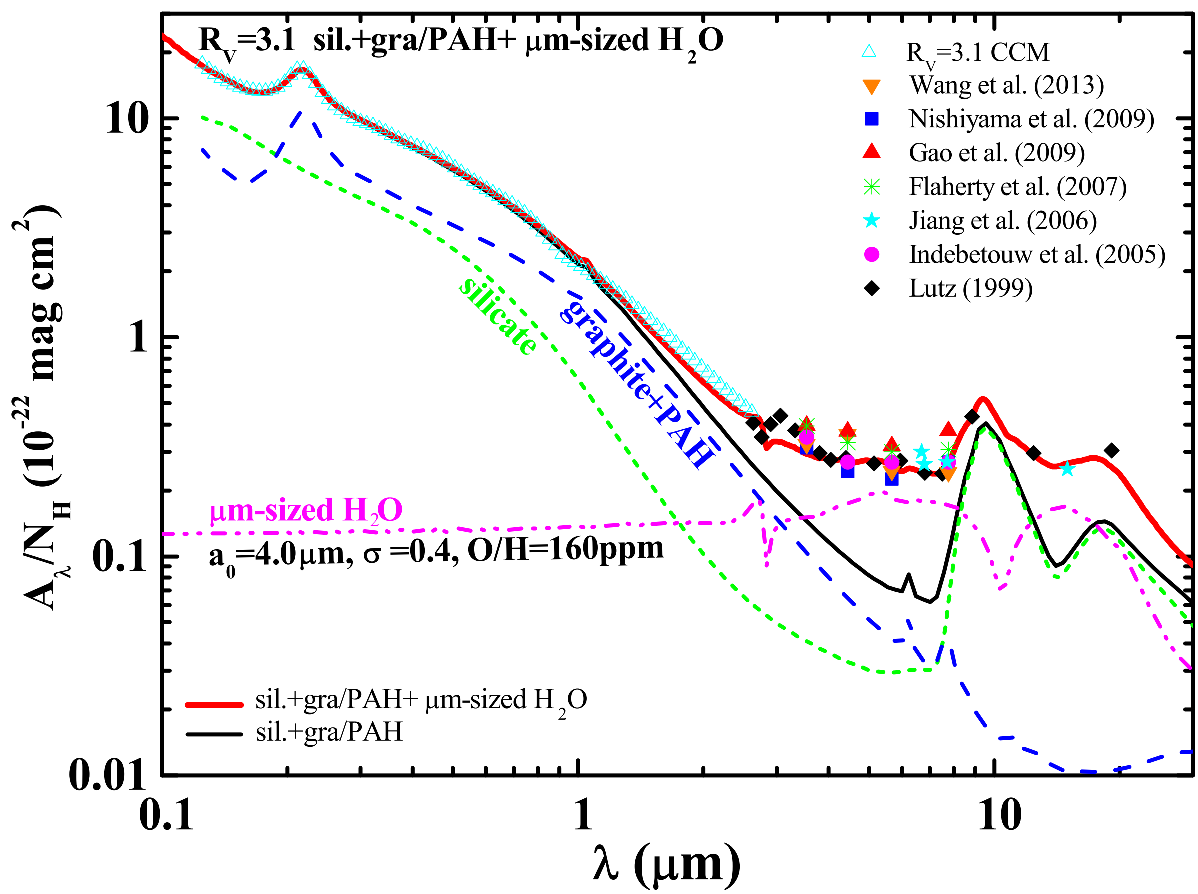

Figure 1. Fitting the $R_{\rm V} = 3.1$ extinction curve from the UV/optical to the near- and mid-IR with (1) amorphous silicate (green short dashed line), (2) graphite and PAHs (blue dashed line), and (3) μm-sized H_2O ice grains (magenta dash-dot-dotted line) of O/H = 160 ppm with a log-normal size distribution characterized by $a_0 \approx 4.0\,\mu$m and $\sigma \approx 0.4$. The thick red solid line plots the model fit which is the sum of silicate, graphite/PAHs, and μm-sized H_2O ice. The black solid line plots the sum of silicate and graphite/PAHs. The symbols plot the observed extinction: the cyan open triangles plot the $R_{\rm V} = 3.1$ UV/optical/near-IR extinction, and the other symbols plot the mid-IR extinction (see text).

$1\,\mu$m $< \lambda < 7\,\mu$m (Draine 1989) which is too steep to be consistent with the subsequent observations made by *ISO* and *Spitzer* since numerous observations suggest that the mid-IR extinction at $3\,\mu$m $< \lambda < 8\,\mu$m is flat or "gray" for both diffuse and dense environments (see Figure 1), including the Galactic center (Lutz 1999, Nishiyama et al. 2009), the Galactic plane (Indebetouw et al. 2005, Jiang et al. 2006, Gao et al. 2009), the Coalsack nebula (Wang et al. 2013), and nearby star-forming regions (Flaherty et al. 2007). All these observations appear to suggest an "universally" flat mid-IR extinction law, with little dependence on environments.

We construct an "observed" extinction curve for the diffuse ISM as follows: (i) for $0.125\,\mu$m $< \lambda < 3\,\mu$m, we take the Galactic average of $R_V = 3.1$ as parameterized by CCM and divide it into 95 wavelengths, equally-spaced in $\ln \lambda$; (ii) for the mid-IR extinction at $3\,\mu$m $< \lambda < 8\,\mu$m, we first obtain a weighted "average" from the observed extinction shown in Figure 1, with twice as much weight given to the diffuse sightlines toward the Galactic center,[5] we then interpolate the "average" mid-IR extinction into 25 logarithmically equally-spaced wavelengths.

We aim at reproducing the observed extinction from the UV/optical to the near- and mid-IR with a mixture of amorphous silicate dust and carbonaceous dust as well as H_2O ice grains. The UV/optical extinction is predominantly caused by sub-μm- and nano-sized grains (Li 2004). The nonde-

[5] The extinction along the line of sight toward the Galactic center is believed to be dominated by dust in the diffuse ISM as revealed by the detection of the $3.4\,\mu$m aliphatic C–H absorption feature which is absent in dense regions (Sandford et al. 1991, Pendleton et al. 1994, Tielens et al. 1996). However, it does contain molecular cloud materials as revealed by the detection of the 3.1 and $6.0\,\mu$m H_2O ice absorption features, e.g., the sightline toward the Galactic center source Sgr A* suffers ~ 30 mag of visual extinction (McFadzean et al. 1989), to which molecular clouds may contribute as much as ~ 10 mag (Whittet et al. 1997). As shown in Figure 1, the ~ 3–$8\,\mu$m extinction curve of the Galactic center (Lutz 1999, Nishiyama et al. 2009) is less flatter than that of other regions. When constructing the "observed" extinction curve, if one assigns less weight to the Galactic center sightlines, one would obtain an even flatter ~ 3–$8\,\mu$m extinction law. Therefore, even more O/H could be tied up in μm-sized H_2O ice grains.

tection of the 3.1 μm absorption feature of H_2O ice in the diffuse ISM places an upper limit of ~ 2 ppm (Whittet et al. 1997) and ~ 9 ppm (Poteet et al. 2015) of O/H in sub-μm-sized H_2O ice grains toward Cyg OB2 No. 12 and ζ Oph, respectively. Therefore, the observed UV/optical extinction is mainly produced by the silicate and carbonaceous components while the H_2O ice component, if present in the diffuse ISM, must be larger than $\sim 1\,\mu$m and cause extinction at $\lambda \gtrsim 1\,\mu$m.

Following Weingartner & Draine (2001; WD01), we model the observed extinction in the wavelength range of $0.125\,\mu\mathrm{m} < \lambda < 8\,\mu\mathrm{m}$ in terms of the silicate-graphite-PAH model combined with a population of μm-sized H_2O ice grains. We take the size distribution functional form of WD01 for the silicate and graphitic component, assuming the latter extends from grains with graphitic properties at radii $a \gtrsim 50$ Å, down to grains with PAH-like properties at very small sizes (see Li & Draine 2001). The dielectric functions of amorphous silicate, graphite, and H_2O ice are taken from Draine & Lee (1984) and Warren (1984). The WD01 model employs two log-normal size distributions for two populations of PAHs which respectively peak at $a_{0,1}$, $a_{0,2}$ and have a width of σ_1, σ_2, consuming a C abundance of $b_{\rm C,1}$, $b_{\rm C,2}$ (per H nuclei). Following Draine & Li (2007), we adopt $a_{0,1} = 3.5$ Å, $\sigma_1 = 0.40$, $b_{\rm C,1} = 45$ ppm, $a_{0,2} = 20$ Å, $\sigma_2 = 0.55$, and $b_{\rm C,2} = 15$ ppm. These parameters were constrained by the observed near- and mid-IR emission. For the μm-sized H_2O ice component, we also adopt a log-normal size distribution of peak size a_0 and width σ:

$$\frac{1}{n_{\rm H}}\frac{dn}{da} = \frac{3}{(2\pi)^{3/2}} \times \frac{\exp\left(-4.5\sigma^2\right)}{\rho_{\rm ICE} a_0^3 \sigma} \times \frac{b_{\rm ICE}\mu_{\rm ICE} m_{\rm H}}{2} \times \frac{1}{a}\exp\left\{-\frac{1}{2}\left[\frac{\ln(a/a_0)}{\sigma}\right]^2\right\}, \tag{1}$$

where $m_{\rm H}$ is the atomic H mass, $\rho_{\rm ICE}$ and $\mu_{\rm ICE}$ are respectively the mass density and the molecular weight of H_2O ice ($\rho_{\rm ICE} \approx 1.0\,{\rm g\,cm^{-3}}$ and $\mu_{\rm ICE} \approx 18$), and $b_{\rm ICE}$ is the O abundance per H nuclei locked up in μm-sized H_2O ice grains.

Following WD01, we use the Levenberg-Marquardt method (Press et al. 1992) to minimize the fitting error between the observed and model extinction (see Wang, Li & Jiang 2015). As shown in Figure 1, together with silicate, graphite and PAHs, H_2O ice grains with $a_0 \approx (4.0 \pm 1.0)\ \mu$m, $\sigma \approx (0.4 \pm 0.1)$, and $b_{\rm ICE} = 160$ ppm of O/H satisfactorily reproduce the $\sim$3–8 μm mid-IR extinction. Figure 1 also shows that these μm-sized H_2O ice grains are "gray" in the UV/optical and make negligible contribution to the observed UV/optical extinction. The size distributions of the silicate and graphite components which closely reproduce the observed UV/optical extinction are characterized by the following parameters: $C_{\rm g} \approx 5.75 \times 10^{-12}$, $\alpha_{\rm g} \approx -1.40$, $\beta_{\rm g} \approx 0.0291$, $a_{\rm t,g} \approx 0.00818\,\mu$m, and $a_{\rm c,g} \approx 0.173\,\mu$m for graphite, $C_{\rm s} \approx 7.56 \times 10^{-14}$, $\alpha_{\rm s} \approx -2.19$, $\beta_{\rm s} \approx -0.586$, $a_{\rm t,s} \approx 0.204\,\mu$m, and $a_{\rm c,s} = 0.1\,\mu$m for silicate (see WD01 for the definition of each parameter).

The model extinction does not show the 3.1 μm absorption feature which is absent in the diffuse ISM. However, it exhibits a narrow, minor structure at $\sim 2.8\,\mu$m arising from the scattering of the O–H stretch of H_2O ice. The extinction toward the Galactic center derived by Lutz (1999) based on the recombination lines of atomic H was not sufficiently resolved in wavelength to rule out this structure. We note that Whittet et al. (1997) reported the detection of a shallow feature centered at $\sim 2.75\,\mu$m in the near-IR spectrum of Cygnus OB2 No. 12 obtained by the *Kuiper Airborne Observatory* (KAO) and *ISO*/SWS. They tentatively attributed this feature to the OH groups of hydrated silicates. However, it was later found to be an artifact caused by the calibration uncertainty (see Whittet et al. 2001).

3 INFRARED EMISSION

To examine whether the model, with the inclusion of a population of μm-sized H_2O ice grains, will result in too much emission in the far-IR, we calculate the equilibrium temperatures of silicate and graphite grains of radii larger than ~ 250 Å as well as μm-sized H_2O ice grains heated by the Mathis, Mezger, & Panagia (1983, MMP83) interstellar radiation field (ISRF; see Figure 2). We also calculate the temperature probability distribution functions of PAHs, small graphite and silicate grains of radii smaller than ~ 250 Å since the heat contents of these ultrasmall grains are smaller than or comparable to the energy of a single UV photon and therefore, they will be transiently heated and will not attain an equilibrium temperature (see Draine & Li 2001).

For a given size, H_2O ice grains are colder than silicate and graphite grains (e.g., $T \approx 14.3$, 15.5, 19.7 K for H_2O ice, silicate and graphite grains of $a = 0.1\,\mu$m, respectively). For a given composition, the dust temperature decreases as the grain size increases (see Figure 2). The best-fit H_2O ice grains of radii of $\sim 4\,\mu$m have an equilibrium temperature of ~ 8.9 K. As shown in Figure 3, these grains mainly emit at $\lambda \gtrsim 200\,\mu$m.

Figure 3 presents the model IR emission which combines the contributions from silicate grains, graphite/PAH grains, and H_2O ice grains. We compare the model IR emission with the diffuse ISM observed by *Planck* and the *Diffuse Infrared Background Experiment* (DIRBE) and the *Far Infrared Absolute Spectrophotometer* (FIRAS) instruments aboard the *Cosmic Background Explorer* (COBE). Figure 3 shows that the model closely fits the observed emission from the near-IR to the far-IR and millimeter (mm). The μm-sized H_2O ice component is "gray" in the UV/optical (see Figure 1) and does not absorb much and therefore by implication, it does not emit much in the far-IR. Although the mass of the μm-sized H_2O ice component exceeds that of graphite/PAHs by $\sim 7\%$, the UV/optical extinction contributed by the former is smaller than that of the latter by a factor of ~ 50. Moreover, the UV/optical extinction of H_2O ice grains is dominated by scattering, instead of absorption. The silicate-graphite/PAH-ice model results in a total IR intensity of $\sim 4.48 \times 10^{-24}\,{\rm erg\,s^{-1}\,H^{-1}}$. The fractional contributions of silicate, graphite/PAHs, and H_2O ice are approximately 27.9%, 71.7%, and 0.34%, respectively.

4 DISCUSSION

We have shown in §2 and §3 that the diffuse ISM has no problem in accommodating the unaccounted for ~ 160 ppm

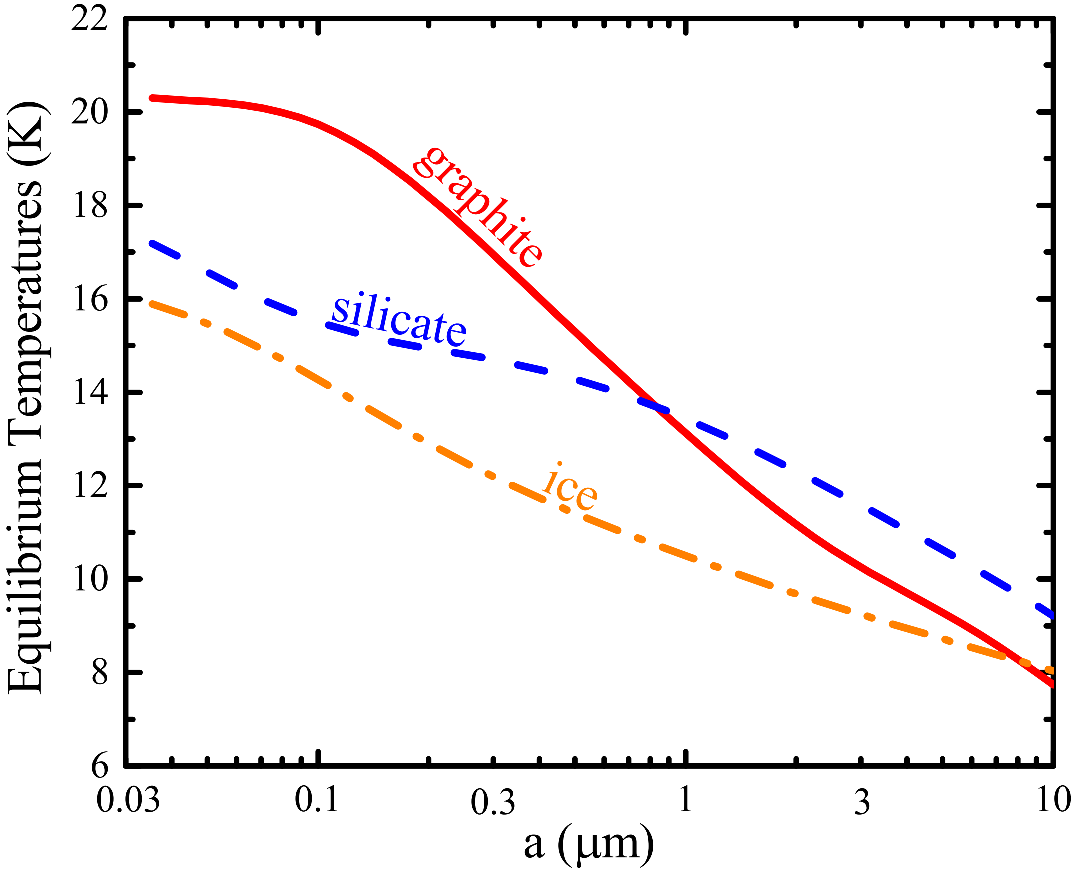

Figure 2. Equilibrium temperatures for graphite (red solid line), silicate (blue dashed line), and H_2O ice grains (orange dash-dotted line) heated by the MMP83 ISRF.

of O/H. With the missing ~ 160 ppm of O/H tied up in μm-sized H_2O ice grains, the silicate-graphite/PAH-ice model closely reproduces the observed extinction from the far-UV to the mid-IR (see Figure 1) as well as the observed thermal emission from the near-IR to the submm/mm wavelengths (see Figure 3). However, the "C crisis" still persists. The model requires $[C/H]_{dust} \approx 225$ ppm to be depleted in graphite/PAHs (with ~ 60 ppm of C/H in PAHs, see Li & Draine 2001). With the gas-phase C/H abundance of $[C/H]_{gas} \approx 140$ ppm (Cardelli et al. 1996) or $[C/H]_{gas} \approx 100$ ppm (Sofia et al. 2011) included, the total required C/H abundance becomes C/H ≈ 365 ppm or C/H ≈ 325 ppm, exceeding that of solar ($[C/H]_{\odot} \approx 269 \pm 31$ ppm, Asplund et al. 2009), proto-Sun ($[C/H]_{\odot} \approx 288 \pm 27$ ppm, Lodders 2003), and early B stars ($[C/H]_{\star} \approx 214 \pm 20$ ppm, Nieva & Przybilla 2012). We note that the shortage of C/H is true for all dust models (e.g., Zubko et al. [2004; ZDA] required $[C/H]_{dust} \approx 244$ ppm, Jones et al. [2013] required $[C/H]_{dust} \approx 233$ ppm). Mathis (1996) argued that porous dust is more effective in absorbing starlight than compact dust and therefore one might require fewer C atoms to account for the observed extinction. However, Li (2005a) showed that, through an analysis based on the Kramers-Kronig relation of Purcell (1969), models invoking porous dust cannot appreciably lower the C/H consumption. A likely solution to the C crisis problem is that the stellar photospheric abundances may be considerably lower than that of the interstellar material from which young stars are formed (see Li 2005a). Alternatively, if the interstellar C/H abundance is like the *current* protosolar abundance of C/H~ 339 ppm (Asplund 2009) when taking into account the Galactic chemical enrichment over the past 4.6 Gyr (Chiappini, Romano, & Matteucci 2003), with $[C/H]_{gas} \approx 100$ ppm (Sofia et al. 2011) subtracted, the available C/H abundance (~ 239 ppm) is approximately consistent with the latest dust models and the so-called C-crisis will be alleviated.

The silicate-graphite/PAH-ice model requires $[Si/H]_{dust} \approx [Mg/H]_{dust} \approx 40.4$ ppm to be depleted in silicate dust. Here we assume a stoichiometric composition of $MgFeSiO_4$ for the silicate dust which depletes all the Si, Mg, and Fe atoms. For Si, it is higher than that of solar ($[Si/H]_{\odot} \approx 32.4 \pm 2.2$ ppm, Asplund et al. 2009) and early B stars ($[Si/H]_{\star} \approx 31.6 \pm 3.6$ ppm, Nieva & Przybilla 2012), it is consistent with the proto-Sun abundance of Si/H $\approx 40.7 \pm 1.9$ ppm (Lodders 2003). In contrast, the Jones et al. (2013) model consumed $[Si/H]_{dust} \approx 50$ ppm. While the ZDA model used fewer Si atoms ($[Si/H]_{dust} \approx 36$ ppm) than the WD01 model ($[Si/H]_{dust} \approx 48$ ppm), the former produces much elss extinction at $\lambda > 1\,\mu$m than the latter (see Figure 23.11 in Draine 2011).

Historically, ices were among the first grain species suggested to be present in the ISM and responsible for the

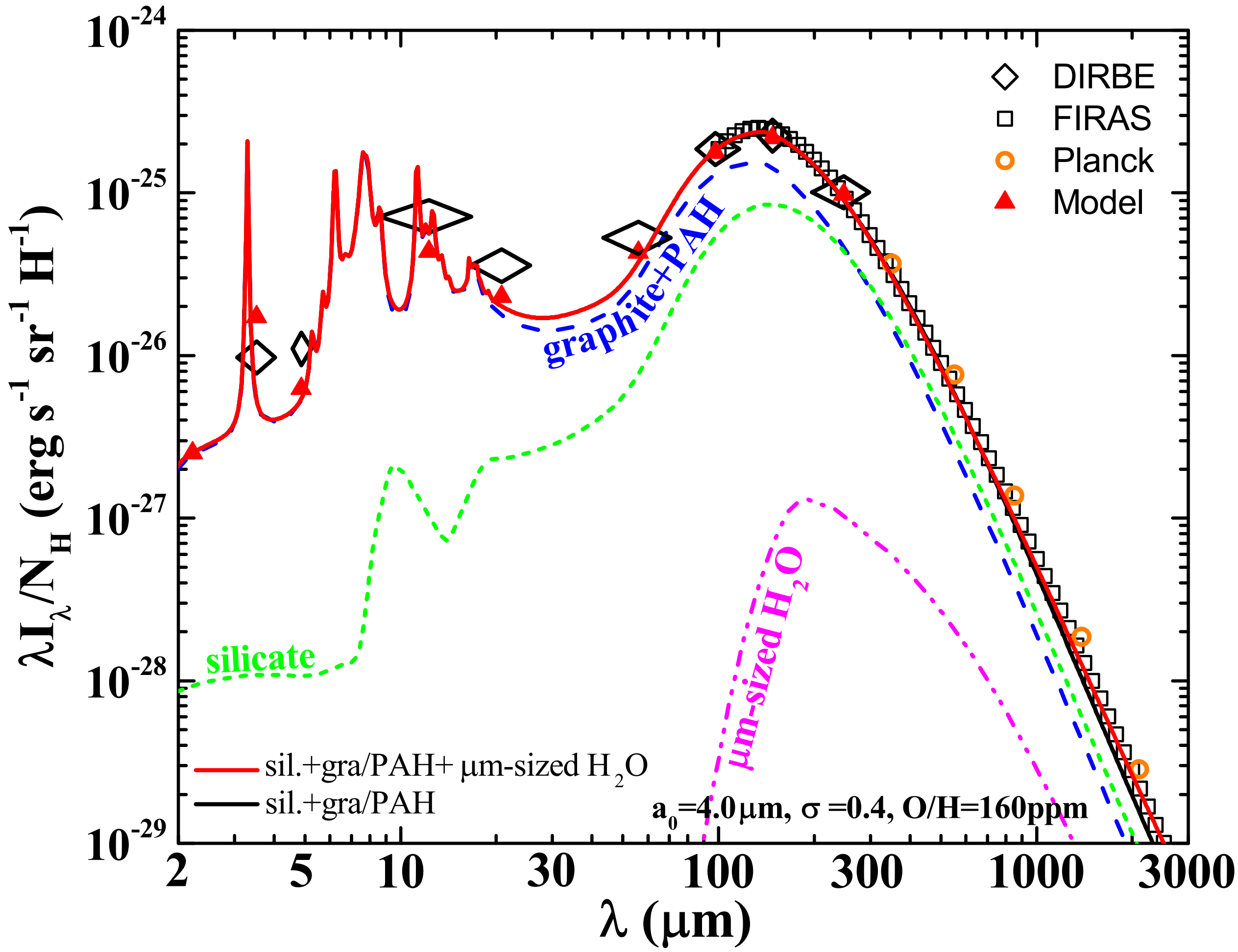

Figure 3. Comparison of the observed emission from the diffuse ISM (black diamonds, black squares, and orange circles) to the model which is the sum of silicate (green short dashed line), graphite/PAHs (blue dashed line), and μm-sized H_2O ice grains (magenta dash-dot-dotted line). Red triangles show the model spectrum (red solid line) convolved with the *DIRBE* filters. Observational data are from *DIRBE* (black diamonds; Arendt et al. 1998), *FIRAS* (black squares; Finkbeiner et al. 1999), and *Planck* (orange circles; Planck Collaboration XVII 2014).

observed extinction (see Li 2005b). Oort & van de Hulst (1946) proposed the "dirty ice" model consisting of saturated molecules such as H_2O, CH_4, and NH_3. In the 1960s, the first attempt to search for the 3.1μm feature of H_2O ice in the diffuse ISM was unsuccessful (Danielson et al. 1965, Knacke et al. 1969). This led to the abandonment of the "dirty ice" model and the proposition of "organic refractory" resulting from the photoprocessing of "dirty ices" as an interstellar grain component (Greenberg et al. 1972, 1995).[6] Based on the then "surplus" of O, C, N elements, Greenberg (1974) speculated that these "excessive" elements could be bound in "interstellar snowballs" ranging in size from baseballs to comets. To the best of our knowledge, the ZDA model is the only contemporary model in which sub-μm-sized H_2O ice was included as a grain component and accounted for $\sim 4.4\%$ of the total dust mass.

A crucial issue for the hypothesis of μm-sized H_2O ice grains as the reservoir of the missing O atoms is how they form and survive in the ISM. In dense molecular clouds, H_2O forms through hydrogenation of O on the surfaces of sub-μm-sized silicate and carbonaceous grains and in this way, a thick ice mantle could be built up (Boogert et al. 2015).[7] In contrast, ice mantles cannot be built up in the diffuse ISM since they will be rapidly removed by photosputtering (Barlow 1978a,b; Draine & Salpeter 1979). We note that in the diffuse ISM, not only H_2O ice but also silicate and graphite are destroyed at a rate faster than their production (McKee 1989). This led Draine (1990) to conclude that the

[6] The core-mantle model of Li & Greenberg (1997) assumes that the silicate core is coated by a mantle of organic refractory material. Whittet (2010b) suggested that the organic refractory matter may potentially account for some of the missing O atoms.

[7] One would expect an ice grain to have a sub-μm-sized nucleation core of silicate or graphite. But for the μm-sized ice grains of interest here, the effects of the core on the extinction and emission are negligible since the core only accounts for $\sim (0.1/4)^3 \approx 1.6 \times 10^{-5}$ of the volume of a grain of $a = 4\,\mu$m.

bulk of the solid material in grains actually condensed in the ISM rather than in stellar outflows. Draine (1990) argued that there must be rapid exchange of matter between the diffuse ISM and molecular clouds since the bulk of grain growth can proceed rapidly only in dense regions. Depending on the posited mass exchange scenario, this implies a turnover time ($\tau_{\rm MC}$) of $\sim 3\times10^6$–2×10^7 yr for molecular clouds (Draine 1990). If the photosputtering lifetimes ($\tau_{\rm pd}$) of μm-sized H_2O ice grains are not shorter than $\tau_{\rm MC}$, the ice grain model might be viable: before they are destroyed by photosputtering, very large ice grains in the diffuse ISM are continuously replenished by the freshly-condensed ice grains formed in dense molecular clouds through accretion and coagulation.

Let $Y_{\rm pd}(\lambda)$ be the photosputtering yield of H_2O ice (i.e., the number of H_2O molecules desorbed per absorbed UV photon of wavelength λ). We derive the photodesorption rate of H_2O ice as following:

$$\dot{N} \equiv dN/dt = \int Y_{\rm pd}(\lambda) \frac{C_{\rm abs}(a,\lambda)\times 4\pi J_\lambda}{hc/\lambda}\, d\lambda \quad , \qquad (2)$$

where h is the Planck constant, c is the speed of light, $C_{\rm abs}(a,\lambda)$ is the absorption cross section of H_2O ice grain of radius a at wavelength λ, and J_λ is the intensity of the MMP83 ISRF. We calculate the photosputtering lifetimes of H_2O ices of radii a from

$$\tau_{\rm pd}(a) = \frac{1}{\dot{N}} \frac{4\pi a^3\, \rho_{\rm ICE}}{3\mu_{\rm ICE} m_{\rm H}} \quad . \qquad (3)$$

Westley et al. (1995) experimentally measured the photodesorption yield of H_2O ice exposed to Lyman-α photons (10.2 eV or 1216 Å) at temperature T to be $Y_{\rm pd} \approx Y_0 + Y_1 \exp(-E/kT)$, where k is the Boltzmann constant, $Y_0 = 0.035 \pm 0.002$, $Y_1 = 0.13 \pm 0.10$, and $E = (29 \pm 6) \times 10^{-3}$ eV. For H_2O ice grains of radii $a = 4\,\mu$m and temperature $T = 8.9$ K (see Figure 2), we estimate the photosputtering lifetime to be $\tau_{\rm pd} \approx 5.8\times10^6$ yr in the diffuse ISM. This lifetime may be underestimated since the photodesorption yield of Westley et al. (1995) could have been overestimated as their data were obtained through laser beam irradiation which might have induced local point heating and thus adding some sublimation to the pure sputtering effect. More recently, Öberg et al. (2009) experimentally determined the photodesorption yields of H_2O ice using a hydrogen discharge lamp ($\sim$7–10.5 eV). They derived an average photodesorption yield of $Y_{\rm pd} \approx 1.3\times10^{-3} + 3.2\times10^{-5}\times T$. This gives a photosputtering lifetime of $\tau_{\rm pd} \approx 7.4\times10^6$ yr for H_2O ice grains of $a = 4\,\mu$m at $T = 8.9$ K. Moreover, Andersson et al. (2006) modeled the photodesorption process at the atomic level by simulating the interaction between photons of $\sim$8–9.5 eV and ice surfaces. They estimated the photodesorption yield to be $Y_{\rm pd} \approx 4\times10^{-4}$ for amorphous ice. This leads to a photosputtering lifetime of $\tau_{\rm pd} \approx 2.9\times10^7$ yr for H_2O ice grains of $a = 4\,\mu$m. Therefore, it seems likely that the diffuse-phase μm-sized H_2O ice grains are continuously replenished on a timely fashion by the dense-phase materials through the turnover of molecular clouds within a timescale of $\tau_{\rm MC} \sim 3\times10^6$–$2\times10^7$ yr before they are destroyed by photosputtering in the diffuse ISM. In contrast, a sub-μm-sized ice grain (coated on a silicate or graphite core) responsible for the 3.1 μm absorption feature in dense clouds will be quickly removed by photosputtering in diffuse clouds at a rate faster than that of an $a = 4\,\mu$m ice grain by a factor of $\sim(4/0.1)^3 \approx 6.4\times10^4$.

Finally, we note that the "missing" O atoms do not *all* have to be tied up in H_2O ice grains. As mentioned earlier, some of the "missing" O atoms could be hidden in organic refractories (Whittet 2010b). On the other hand, the observed flat extinction at $\sim$3–8 μm could also *partly* be caused by other dust components, e.g., μm-sized graphite (see Wang, Li, & Jiang 2015).

5 SUMMARY

While the ISM seems to be short of the element C to form a sufficient amount of carbonaceous dust (together with silicate dust) to account for the observed extinction, the element O seems overabundant and as many as $\sim$160 O atoms (per 10^6 H atoms) are unaccounted for by their presence in gas and dust. We have examined the hypothesis of μm-sized H_2O ice grains as the reservoir of the missing O atoms. It is found that the diffuse ISM has no difficulty in accommodating $\sim$160 ppm of O/H in μm-sized H_2O ice grains, confirming the earlier suggestions made by Jenkins (2009) and Poteet et al. (2015). With a radius of $\sim 4\,\mu$m, these grains are "gray" in the UV/optical and contribute very little to the UV/optical extinction. The 3.1 μm O–H stretching feature of these grains is significantly suppressed, consistent with the nondetection of this feature in the diffuse ISM. They absorb and scatter effectively in the mid-IR and are capable of accounting for the observed flat extinction at $\sim$3–8 μm. Being relatively transparent in the UV/optical, they do not absorb much and therefore they are cold and mainly emit in the far-IR at $\lambda \gtrsim 200\,\mu$m, accounting for only $\sim$0.34% of the total IR power of the Galactic diffuse ISM. With a photosputtering lifetime of $\tau_{\rm pd} \approx 5.8\times10^6$–$2.9\times10^7$ yr longer than or comparable to the turnover timescale of molecular clouds of $\tau_{\rm MC} \approx 3\times10^6$–$2\times10^7$ yr implied by the observed large depletions of Si and Fe elements in the diffuse ISM, H_2O ice grains of radii $a \gtrsim 4\,\mu$m could be present in the diffuse ISM through rapid exchange of material between dense molecular clouds where they form and diffuse clouds where they are destroyed by photosputtering.

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